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(54) **Microporous membranes from poly(ether-etherketone)-type polymers and low melting point crystallizable polymers, and a process for making the same.**

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## Description

This invention relates to microporous membranes prepared from poly(etheretherketone)-type polymers and low melting point crystallizable polymers, and a process for making the same. Such membranes are useful in the treatment of liquids by the membrane separation processes of ultrafiltration, microfiltration, macrofiltration, depth filtration, membrane distillation, and membrane stripping. The membranes of this invention are also useful as microporous supports for composite liquid or gas separation membranes.

In the past, microporous membranes have been fabricated from polyolefins such as polyethylene and polypropylene. One typical method of preparing such polyolefin membranes is by an extrusion process which involves dissolving the polyolefin in a solvent or a mixture of solvent and non-solvent, extruding the polyolefin/solvent/non-solvent mixture into membranes, and immersing the membranes into a leach bath. Another method of preparing such polyolefin membranes is by a melt-extrusion process which involves extruding the membranes from the molten polyolefin, followed by cold drawing the membranes. However, polyolefins, while inexpensive and easy to process, exhibit relatively low heat distortion temperatures.

Poly(etheretherketone)-type polymers are high performance thermoplastics which possess high glass transition temperatures, high crystalline melting points, high thermal stability, and high solvent resistance. Such properties make poly(etheretherketone)-type polymers useful for membranes employed in liquid separations, particularly membrane separation processes which involve treatment of organic, acidic, or basic liquids at elevated temperatures.

The very properties which make poly(etheretherketone)-type polymers desirable materials for use in applications which require high temperature and/or solvent resistance also render the polymers very difficult to process into membranes, particularly since poly(etheretherketone)-type polymers exhibit relatively low solution viscosities at membrane fabrication temperatures in excess of 300 °C. Furthermore, poly(etheretherketone)-type polymers are extremely solvent resistant and are therefore considered to be insoluble in all common solvents. Therefore, to form membranes, poly(etheretherketone), for example, is typically dissolved in very strong inorganic acids such as concentrated sulfuric acid to sulfonate the poly(etheretherketone), which renders the sulfonated poly(etheretherketone) soluble in common solvents such as dimethylformamide and dimethylacetamide. The problem associated with such a process is that the fabricated membrane comprises not poly(etheretherketone), but rather sulfonated poly(etheretherketone), which is soluble in common solvents. Thus, the high solvent resistance of poly(etheretherketone) is lost. Furthermore, sulfonated poly(etheretherketone) swells in aqueous solutions, which adversely affects membrane performance in aqueous solution separation applications.

What is needed is a process of preparing microporous membranes from poly(etheretherketone)-type polymers using plasticizers which do not chemically modify or degrade the poly(etheretherketone)-type polymer during fabrication so that the high strength, temperature resistance, and solvent resistance of the unsulfonated poly(etheretherketone)-type polymer is retained by the fabricated membranes. What is further needed is a method of increasing the solution viscosities of the poly(etheretherketone)-type polymers, so that membranes can be more easily fabricated at the high temperatures required for preparing membranes from such polymers.

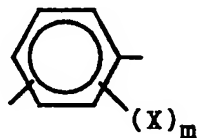
The invention is a process for preparing a microporous membrane from an unsulfonated poly(etheretherketone)-type polymer comprising the steps of:

- A. forming a mixture comprising:
  - (i) at least one unsulfonated poly(etheretherketone)-type polymer,
  - (ii) at least one low melting point crystallizable polymer which is at least partially incompatible with said poly(etheretherketone)-type polymer and which possesses a melting point of less than ( $T_m - 30^\circ\text{C}$ ), wherein  $T_m$  is the melting point of the poly(etheretherketone)-type polymer, and a molecular weight of at least 400, and
  - (iii) optionally, a plasticizer comprising at least one organic compound capable of dissolving at least 10 weight percent of the poly(etheretherketone)-type polymer at the extrusion or casting temperature;
- B. heating said mixture to a temperature at which said mixture becomes a fluid;
- C. extruding or casting said fluid under conditions such that a membrane is formed;
- D. optionally, quenching or coagulating said membrane by passing said membrane through at least one quench or coagulation zone under conditions such that said membrane solidifies; and
- E. optionally, leaching said membrane by passing said membrane through at least one leach zone under conditions such that at least a portion of said low melting point crystallizable polymer, at least a portion of said plasticizer for the unsulfonated poly(etheretherketone)-type polymer, or a combination thereof, is removed from said membrane; and

F. optionally, before leaching, during leaching, after leaching, or a combination thereof, drawing said membrane to increase the flux of fluid through said membrane while said membrane is at a temperature above 25°C and below the crystalline melting point of the poly(etheretherketone)-type polymer or the depressed melting point of said mixture.

The membranes of this invention exhibit excellent solvent and temperature resistance. The membranes also possess high tensile strength. The membranes are useful as microporous membranes for liquid separations such as ultrafiltration, microfiltration, macrofiltration, depth filtration, membrane stripping, and membrane distillation and as microporous supports for composite liquid or gas separation membranes.

Poly(etheretherketone)-type polymers refer to polymers containing predominantly ether, -R-O-R-, and ketone, -R-CO-R-, linkages, wherein R is a divalent aromatic group. R is preferably a substituted or unsubstituted phenylene of Formula 1:



Formula 1

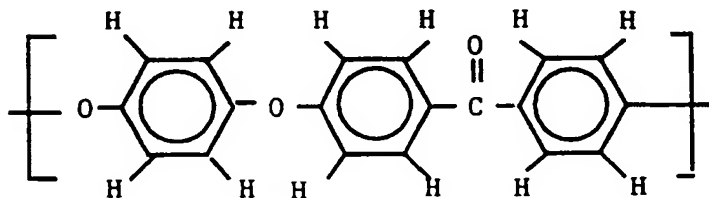
wherein

X is independently in each occurrence hydrogen, a C<sub>1-4</sub> alkyl, or a halogen; and m is an integer between 0 and 4, inclusive.

X is preferably hydrogen, methyl, ethyl, chlorine, bromine, or fluorine.

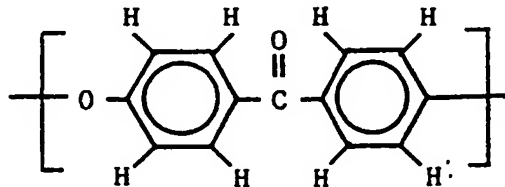
Examples of preferred poly(etheretherketone)-type polymers within the scope of this invention include poly(etherketone) (PEK), poly(aryletherketone) (PAEK), poly(etheretherketone) (PEEK), poly(etherketoneketone) (PEKK), poly(etheretheretherketone) (PEEEK), poly(etheretherketoneketone) (PEEKK), poly(etherketoneetherketoneketone) (PEKEKK), and mixtures thereof.

An especially preferred poly(etheretherketone)-type polymer for use in this invention is PEEK, that is, poly(oxy-p-phenyleneoxy-p-phenylenecarbonyl-p-phenylene). PEEK is comprised of the repeat units described in Formula 2:



Formula 2

Another especially preferred poly(etheretherketone)-type polymer for use in this invention is PEK, that is, poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene). PEK is comprised of the repeat units described in Formula 3:



Formula 3

The poly(etheretherketone)-type polymers useful in this invention are unsulfonated. The poly(etheretherketone)-type polymers from which the membranes are fabricated preferably possess a degree of crystallinity of at least 10 percent, more preferably of at least 20 percent, even more preferably of at least

30 percent, and a melting point of at least 190 °C, more preferably of at least 250 °C.

Commercially available PEEK, for example, VICTREX® PEEK 450 (® trademark of ICI Americas, Inc.), possesses a glass transition temperature of 143 °C and a melting point of 334 °C. Such commercially available PEEK possesses a tensile strength of  $91.8 \cdot 10^6$  N/m<sup>2</sup> (13,300 psi) (ASTM Test Method D638), an elongation at break of 50 percent (ASTM Test Method D638 at 23 °C and test speed of 0.2 in./min.), an ultimate shear strength of  $95.2 \cdot 10^6$  N/m<sup>2</sup> (13,800 psi) (ASTM Test Method D3846), a shear modulus of  $1300.7 \cdot 10^6$  N/m<sup>2</sup> (188,500 psi) (at 23 °C), and a tensile modulus (1 percent secant) of  $3602.5 \cdot 10^6$  N/m<sup>2</sup> (522,100 psi) (ASTM Test Method D638 at 23 °C). The synthesis of such polymers is known in the art. See U.S. Patents 4,320,224 and 4,331,798, the relevant portions relating to polymer synthesis incorporated herein by reference.

The low melting point crystallizable polymers useful in this invention are at least partially incompatible with the poly(etheretherketone)-type polymer. Partially incompatible as used herein means that the low melting point crystallizable polymer is at least partially immiscible and/or partially soluble with the poly(etheretherketone)-type polymer. Preferably the low melting point crystallizable polymer is substantially incompatible or immiscible with the poly(etheretherketone)-type polymer at 25 °C. Incompatibility or immiscibility of the low melting point crystallizable polymer with the poly(etheretherketone)-type polymer may be determined by methods known in the art. See Polymer Blends, Vol. 1, Academic Press, Inc., New York, New York, 1978, pp. 17-20 and Olabisi et al., Polymer-Polymer Miscibility, Academic Press, New York, New York, 1979, pp. 1-17.

The low melting point crystallizable polymers useful in this invention possess a melting point of less than ( $T_m - 30$  °C), preferably of less than ( $T_m - 40$  °C), more preferably of less than ( $T_m - 50$  °C); wherein  $T_m$  is the melting point of the poly(etheretherketone)-type polymer. The low melting point crystallizable polymers useful in this invention possess a melting point or a depressed melting point when mixed with the poly(etheretherketone)-type polymer or with the poly(etheretherketone)-type polymer and plasticizer, of preferably less than 300 °C, more preferably less than 200 °C, even more preferably of less than 100 °C. The low melting point crystallizable polymers useful in this invention possess a molecular weight of at least 400, preferably of at least 500, more preferably of at least 600.

Preferred low melting point crystallizable polymers include poly(caprolactones), poly(ethylene oxide), poly(ethylene glycol), poly(oxymethylene), poly(trimethylene oxide), poly(ethylene glycol)methylether, poly(vinyl alcohol), poly(vinyl chloride), crystalline cellulose esters, poly(caprolactone)diol, and poly(caprolactone)triol. The polymers may contain hydroxy, amine,  $C_1-4$  alkyl, and other end-blocking groups provided that such polymers are crystallizable and possess melting points or depressed melting points and molecular weights as hereinbefore described.

The optional plasticizers useful in this invention comprise at least one organic compound preferably capable of dissolving at least 10 weight percent of the poly(etheretherketone)-type polymer present at the membrane fabrication temperature. The plasticizer more preferably dissolves at the fabrication temperature at least 25 weight percent of the poly(etheretherketone)-type polymer and even more preferably 50 weight percent of the poly(etheretherketone)-type polymer. The plasticizer may be comprised of at least one solvent for the poly(etheretherketone)-type polymer or a mixture of at least one solvent and at least one non-solvent for the poly(etheretherketone)-type polymer, provided the solvent/non-solvent mixture itself is capable of dissolving at least 10 weight percent of the poly(etheretherketone)-type polymer at the membrane fabrication temperature. A solvent for the poly(etheretherketone)-type polymer dissolves at least 10 weight percent poly(etheretherketone)-type polymer at the membrane fabrication temperature. A non-solvent for the poly(etheretherketone)-type polymer dissolves less than 10 weight percent of the poly(etheretherketone)-type polymer at the membrane fabrication temperature.

A preferred class of solvents useful in this invention are organic compounds consisting predominantly of carbon and hydrogen and optionally oxygen, nitrogen, sulfur, halogen, and mixtures thereof, wherein the organic compound has a molecular weight of between 160 and 450, contains at least one six-membered aromatic ring structure, and possesses a boiling point of between 150 °C and 480 °C.

Preferred solvents useful in this invention include diphenic acid, N,N-diphenylformamide, benzil, anthracene, 1-phenylnaphthalene, 4-bromobiphenyl, 4-bromodiphenylether, benzophenone, 1-benzyl-2-pyrrolidinone, o,o'-biphenol, phenanthrene, triphenylmethanol, triphenylmethane, triphenylene, 1,2,3-triphenylbenzene, diphenylsulfone, 2,5-diphenyloxazole, 2-biphenylcarboxylic acid, 4-biphenylcarboxylic acid, m-terphenyl, 4-benzoylbiphenyl, 2-benzoylnaphthalene, 3-phenoxybenzyl alcohol, fluoranthene, 2,5-diphenyl-1,3,4-oxadiazole, 9-fluorenone, 1,2-dibenzoylbenzene, dibenzoylmethane, p-terphenyl, 4-phenylphenol, 4,4'-dibromobiphenyl, diphenylphthalate, 2,6-diphenylphenol, phenothiazine, 4,4'-dimethoxybenzophenone, 9,10-diphenylanthracene, pentachlorophenol, pyrene, 9,9'-bifluorene, a mixture of terphenyls, for example, SANTOWAX R® mixed terphenyls (® trademark of the Monsanto Company), a mixture of partially

hydrogenated terphenyls, for example, THERMINOL 66® partially hydrogenated terphenyls (® trademark of the Monsanto Company), a mixture of terphenyls and quaterphenyls, for example, THERMINOL 75® mixed terphenyls and quaterphenyls (trademark of the Monsanto Company), 1-phenyl-2-pyrrolidinone, 4,4'-isopropylidenediphenol, 4,4'-dihydroxybenzophenone, quaterphenyl, diphenyl terephthalate, 4,4'-dimethyldiphenylsulfone, 3,3',4,4'-tetramethyldiphenylsulfone, and mixtures thereof. Not all of these solvents are  
 5 equally effective with all poly(etheretherketone)-type polymers. One of ordinary skill in the art can readily select the best solvent for a specific polymer empirically.

More preferred solvents include N,N-diphenylformamide, benzil, anthracene, 1-phenylnaphthalene, 4-bromobiphenyl, 4-bromodiphenyl ether, benzophenone, 1-benzyl-2-pyrrolidinone, o,o'-biphenol, phenanthrene, triphenylmethanol, triphenylmethane, triphenylene, 1,2,3-triphenylbenzene, diphenylsulfone, 2,5-diphenyloxazole, 2-biphenylcarboxylic acid, 4-biphenylcarboxylic acid, m-terphenyl, 4-benzoylbiphenyl, 2-benzoylnaphthalene, 3-phenoxybenzyl alcohol, fluoranthene, 2,5-diphenyl-1,3,4-oxadiazole, 9-fluorenone, 1,2-dibenzoylbenzene, dibenzoylmethane, p-terphenyl, 4-phenylphenol, 4,4'-dibromobiphenyl, diphenylphthalate, 2,6-diphenylphenol, phenothiazine, 4,4'-dimethoxybenzophenone, 9,10-diphenylanthracene, pentachlorophenol, pyrene, 9,9'-bifluorene, a mixture of terphenyls, for example, SANTOWAX R® mixed terphenyls  
 10 (® trademark of the Monsanto Company), a mixture of partially hydrogenated terphenyls, for example, THERMINOL 66® partially hydrogenated terphenyls (® trademark of the Monsanto Company), a mixture of terphenyls and quaterphenyls, for example, THERMINOL 75® mixed terphenyls and quaterphenyls (® trademark of the Monsanto Company), 1-phenyl-2-pyrrolidinone, 4,4'-isopropylidenediphenol, 4,4'-dihydroxybenzophenone, quaterphenyl, diphenyl terephthalate, 4,4'-dimethyldiphenylsulfone, 3,3',4,4'-tetramethyldiphenylsulfone, and mixtures thereof.  
 15 20

Even more preferred solvents include triphenylmethanol, triphenylmethane, triphenylene, 1,2,3-triphenylbenzene, diphenylsulfone, 2,5-diphenyloxazole, 2-biphenylcarboxylic acid, 4-biphenylcarboxylic acid, m-terphenyl, 4-benzoylbiphenyl, 2-benzoylnaphthalene, 3-phenoxybenzyl alcohol, fluoranthene, 2,5-diphenyl-1,3,4-oxadiazole, 9-fluorenone, 1,2-dibenzoylbenzene, dibenzoylmethane, p-terphenyl, 4-phenylphenol, 4,4'-dibromobiphenyl, diphenylphthalate, 2,6-diphenylphenol, phenothiazine, 4,4'-dimethoxybenzophenone, 9,10-diphenylanthracene, pentachlorophenol, pyrene, 9,9'-bifluorene, a mixture of terphenyls, for example, SANTOWAX R® mixed terphenyls (® trademark of the Monsanto Company), a mixture of partially hydrogenated terphenyls, for example, THERMINOL 66® partially hydrogenated terphenyls (® trademark of the Monsanto Company), a mixture of terphenyls and quaterphenyls, for example, THERMINOL 75® mixed terphenyls and quaterphenyls (® trademark of the Monsanto Company), 1-phenyl-2-pyrrolidinone, 4,4'-isopropylidenediphenol, 4,4'-dihydroxybenzophenone, diphenyl terephthalate, 4,4'-dimethyldiphenylsulfone, 3,3',4,4'-tetramethyldiphenylsulfone, and mixtures thereof.  
 25 30

Especially preferred solvents include m-terphenyl, p-terphenyl, a mixture of terphenyls, for example, SANTOWAX R® mixed terphenyls (® trademark of the Monsanto Company), a mixture of partially hydrogenated terphenyls, for example, THERMINOL 66® partially hydrogenated terphenyls (® trademark of the Monsanto Company), a mixture of terphenyls and quaterphenyls, for example, THERMINOL 75® mixed terphenyls and quaterphenyls (® trademark of the Monsanto Company), diphenylsulfone, and mixtures thereof.  
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A preferred class of non-solvents useful in this invention are organic compounds consisting predominantly of carbon and hydrogen and optionally oxygen, phosphorus, silicon, nitrogen, sulfur, halogen, and mixtures thereof, wherein the organic compound has a molecular weight of between 120 and 455, and possesses a boiling point of between 150 °C and 480 °C. The non-solvents more preferably have a boiling point of between 280 °C and 480 °C, even more preferably between 300 °C and 480 °C. The non-solvents preferably are soluble in the solvent used at elevated temperatures.  
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Preferred non-solvents useful in this invention include 1,3,5-triphenylbenzene, tetraphenylmethane, tetraphenylsilane, diphenylsulfoxide, 1,1-diphenylacetone, 1,3-diphenylacetone, 4-acetylbiphenyl, 4,4'-diphenylbenzophenone, 1-benzoyl-4-piperidone, diphenyl carbonate, bibenzyl, diphenylmethylphosphate, 1-bromo-naphthalene, 2-phenoxybiphenyl, triphenylphosphate, cyclohexylphenylketone, 1,4-dibenzoylbutane, 2,4,6-trichlorophenol, mineral oil, paraffin oil, petroleum oil, for example, MOBILTHERM 600® heat transfer oil, MOBILTHERM 603® heat transfer oil, MOBILTHERM 605® heat transfer oil (® all trademarks of Mobil Oil Corporation), butyl stearate, 9-phenylanthracene, 2-phenylphenol, 1-ethoxynaphthalene, phenylbenzoate, 1-phenyldecane, 1-methoxynaphthalene, 2-methoxynaphthalene, 1,3-diphenoxybenzene, 1,8-dichloroanthraquinone, 9,10-dichloroanthracene, polyphosphoric acid, 1-chloronaphthalene, diphenylether, 1-cyclohexyl-2-pyrrolidinone, hydrogenated terphenyl, for example, HB-40® hydrogenated terphenyl (® trademark of the Monsanto Company), dioctylphthalate, 5-chloro-2-benzoxazolone, dibenzothiophene, diphenylsulfide, diphenylchlorophosphate, fluorene, sulfolane, methyl myristate, methyl stearate, hexadecane, dimethylphthalate, tetraethylene glycol dimethylether, diethylene glycol dibutylether, docosane, eicosane, dotriacon-  
 50 55

tane, 2,7-dimethoxynaphthalene, 2,6-dimethoxynaphthalene, o-terphenyl, 1,1-diphenylethylene, epsilon-caprolactam, thianthrene, silicone oil, for example, DC-704® silicone oil and DC-710® silicone oil (® trademarks of Dow-Corning Corporation), and mixtures thereof.

More preferred non-solvents include 1,3,5-triphenylbenzene, tetraphenylmethane, tetraphenylsilane, 5 diphenylsulfoxide, 1,1-diphenylacetone, 1,3-diphenylacetone, diphenylcarbonate, diphenylmethylphosphate, 2-phenoxybiphenyl, butyl stearate, 9-phenylanthracene, 1-cyclohexyl-2-pyrrolidinone, mineral oil, paraffin oil, petroleum oil, for example, MOBILTHERM 600® heat transfer oil, MOBILTHERM 603® heat transfer oil, MOBILTHERM 605® heat transfer oil (® all trademarks of Mobil Oil Corporation), HB-40® hydrogenated 10 terphenyl (® trademark of the Monsanto Company), dioctylphthalate, dibenzothiophene, diphenylchlorophosphate, methyl myristate, methyl stearate, docosane, eicosane, dotriacontane, o-terphenyl, thianthrene, silicone oil, for example, DC-704® silicone oil and DC-710® silicone oil (® trademarks of Dow-Corning Corporation), and mixtures thereof.

Even more preferred non-solvents include 1,3,5-triphenylbenzene, tetraphenylmethane, tetraphenylsilane, diphenylsulfoxide, 2-phenoxybiphenyl, butyl stearate, 9-phenylanthracene, dioctylphthalate, methyl 15 stearate, docosane, dotriacontane, thianthrene, mineral oil, paraffin oil, petroleum oil, for example, MOBILTHERM 600® heat transfer oil, MOBILTHERM 603® heat transfer oil, MOBILTHERM 605® heat transfer oil (® all trademarks of Mobil Oil Corporation), and mixtures thereof.

The concentrations of the components in the mixture may vary and are dependent upon the desired membrane characteristics, such as porosity and pore size, and the fabrication method. The concentrations 20 of poly(etheretherketone)-type polymer, the low melting point crystallizable polymer, and the optional plasticizer in the mixture is that which result in a mixture with a suitable viscosity for extrusion or casting at the membrane fabrication temperature. The viscosity of the mixture must not be so high that the fluid is too viscous to fabricate; the viscosity must not be too low such that the membrane lacks physical integrity. Extrusion mixtures of poly(etheretherketone)-type polymers, low melting point crystallizable polymers, and 25 optional plasticizers generally possess non-Newtonian viscosity behavior; therefore, such mixtures exhibit a shear rate dependence upon viscosity. The mixture preferably has a viscosity at extrusion temperatures of between 100 and 10,000 poise at a shear rate of from 10 to 10,000 sec<sup>-1</sup>, more preferably between 200 and 1,000 poise at a shear rate of from 50 to 1,000 sec<sup>-1</sup>.

The concentration of poly(etheretherketone)-type polymer in the mixture is preferably from 10 to 90 30 weight percent, more preferably from 20 to 80 weight percent, even more preferably from 25 to 75 weight percent.

The concentration of low melting point crystallizable polymer in the mixture is preferably from 3 to 80 weight percent, more preferably from 3 to 70 weight percent, even more preferably from 3 to 65 weight percent.

35 The membranes of this invention may be prepared by casting or extrusion. In the casting process, the polymers are optionally mixed with the plasticizer comprising at least one solvent and optionally at least one non-solvent for the polymers at elevated temperatures. The elevated temperature at which the mixture is mixed is that temperature at which the mixture is a fluid, and below that temperature at which the polymers degrade and below that temperature at which the optional plasticizer comprising solvent and optional non-solvent boils. The upper temperature limit is preferably below 360 °C, more preferably below 345 °C, even 40 more preferably below 330 °C. The minimum temperature limit is preferably at least 25 °C. The contacting takes place with adequate mixing or agitation.

In the case of casting, a membrane may be cast into flat sheet form by pouring the fluid mixture onto a smooth support surface and drawing down the fluid mixture to an appropriate thickness with a suitable tool 45 such as a doctor blade or casting bar. Alternately, the fluid mixture may be cast in a continuous process by casting the fluid mixture onto endless belts or rotating drums. The casting surface may be such that the membrane may thereafter be readily separated from the surface. For example, the membrane may be cast onto a support having a low surface energy, such as silicone, coated glass, Teflon, or coated metal, or a surface to which the membrane will not adhere. Alternately, the fluid mixture may be cast onto a support 50 surface which may thereafter be dissolved away from the finished membrane. The fluid mixture may also be cast onto a porous support surface. The cast membrane is thereafter subsequently quenched or coagulated, leached, and optionally drawn as described hereinafter for membranes formed by the extrusion process.

Membranes may be extruded from the poly(etheretherketone)-type polymer mixtures hereinbefore 55 described. The components of the extrusion mixture may be combined prior to extrusion by mixing in any convenient manner with conventional mixing equipment, as for example, in a Hobart brand mixer. The components of the extrusion mixture may also be combined and mixed under heating in a resin kettle. Alternately, the extrusion mixture may be prepared by extruding the components through a twin screw

extruder, cooling the extrudate, and grinding or pelletizing the extrudate to a particle size readily fed to a single or twin screw extruder. Alternately, the components of the extrusion mixture may be combined directly in a melt-pot or twin screw extruder and extruded into a membrane in a single step. Static mixers may be employed.

5 The mixture is heated to a temperature which results in a fluid possessing a viscosity suitable for extrusion. The temperature should not be so high or the exposure time so long as to cause significant degradation of the poly(etheretherketone)-type polymer, the low melting point crystallizable polymer, and/or the optional plasticizer. The temperature should not be so low as to render the fluid too viscous to extrude. The extrusion temperature is preferably between 100°C and 400°C, more preferably between 110°C and 10 380°C, even more preferably between 120°C and 370°C.

The mixture of polymers and optional plasticizer is extruded through a film, tube, or hollow fiber die (spinnerette). Hollow fiber spinnerettes typically are multi-holed and thus produce a tow of multiple fibers. The hollow fiber spinnerettes include a means for supplying fluid to the core of the extrudate. The core fluid is used to prevent the collapsing of the hollow fibers as they exit the spinnerette. The core fluid may be a 15 gas such as nitrogen, air, carbon dioxide, or other inert gas or a liquid which is a non-solvent for the polymers. Examples of suitable core liquids include dioctylphthalate, methyl stearate, polyglycol, mineral oil, paraffin oil, petroleum oil, for example, MOBILTHERM® 600, 603, and 605 heat transfer oils (® trademarks of Mobil Oil Corporation), and silicone oil, for example, DC-704® and DC-710® silicone oil (® trademarks of Dow-Corning Corporation). Use of a liquid non-solvent as the core fluid may result in a microporous 20 membrane with an inside skin. A solvent and non-solvent core liquid mixture may be used to control the inside skin morphology. A non-solvent fluid may optionally be used on the outside of the hollow fiber membrane to produce an outside skin.

The extrudate exiting the die enters one or more quench or coagulation zones. The environment of the quench or coagulation zone may be gaseous or liquid. Within the quench or coagulation zone, the extrudate 25 is subjected to cooling and/or coagulation to cause solidification of the membrane with the optional simultaneous removal of a portion of the plasticizer and/or low melting point crystallizable polymer.

In a preferred embodiment, the membrane is initially quenched in a gaseous environment such as air, nitrogen, or other inert gas. The temperature of the gaseous quench zone is that temperature at which solidification occurs at a reasonable rate. The temperature of the gaseous quench zone is preferably in the 30 range of from 0°C to 275°C, more preferably in the range of from 5°C to 150°C, even more preferably in the range of from 10°C to 90°C. The residence time in the gaseous quench zone is that which is sufficient to solidify the membrane. The residence time in the gaseous quench zone is preferably at least 0.01 seconds, more preferably at least 0.05 seconds. The residence time in the gaseous quench zone is preferably less than 300 seconds, more preferably less than 120 seconds, even more preferably less than 90 seconds. Shrouds may be used to help control gaseous flowrates and temperatures within the gaseous 35 quench zone.

Following or instead of the gaseous quench, the membrane may optionally be quenched or coagulated in a liquid environment which is substantially a non-solvent for the poly(etheretherketone)-type polymer, such as water, ethylene glycol, or glycerol, and which optionally contains an effective amount of a swelling 40 agent. The temperature of the quench or coagulation liquid is that temperature at which the membrane is not adversely affected and at which solidification occurs at a reasonable rate. The quench or coagulation liquid temperature is preferably between 0°C and 275°C, more preferably between 5°C and 250°C, even more preferably between 10°C and 225°C. The residence time in the liquid quench zone is that which is sufficient to solidify the membrane. The residence time in the liquid quench zone is preferably at least 0.01 45 seconds, more preferably at least 0.05 seconds. The residence time in the liquid quench zone is preferably less than 300 seconds, more preferably less than 120 seconds, even more preferably less than 90 seconds.

Following quenching and/or coagulation, the membrane may be passed through one or more leach zones to remove at least a portion of the low melting point crystallizable polymer, at least a portion of the plasticizer, or a combination thereof. The leach zone need not remove all of the plasticizer and/or low 50 melting point crystallizable polymer from the membrane. The leach zone preferably removes a substantial portion of the plasticizer and/or low melting point crystallizable polymer. Preferably, the leach zone removes the plasticizer to a level of less than 5.0 weight percent in the leached membrane, more preferably less than 2.0 weight percent in the leached membrane. Preferably, the leach zone removes the low melting point crystallizable polymer to a level of less than 5.0 weight percent in the leached membrane, more preferably 55 less than 2.0 weight percent in the leached membrane.

The leach zone is comprised of a liquid which is a non-solvent for the poly(etheretherketone)-type polymer but which is a solvent for the plasticizer and/or low melting point crystallizable polymer. Preferred leach liquids include toluene, xylene, acetone, water, and chlorinated hydrocarbons such as methylene



chloride, carbon tetrachloride, trichloroethylene, and 1,1,1-trichloroethane. The leach liquid may also comprise an acid or alkali aqueous solution if an acid or alkali soluble solvent and optional non-solvent for the poly(etheretherketone)-type polymer are used in the extrusion or casting mixture.

The maximum temperature of the leach bath is that temperature at which the membrane is not adversely affected. The minimum temperature of the leach bath is that temperature at which plasticizer removal from the membrane occurs at a reasonable rate. The temperature of the leach bath is preferably between 0°C and 250°C, more preferably between 5°C and 200°C, even more preferably between 10°C and 150°C. The residence time in the leach bath is preferably long enough to remove at least a portion of the plasticizer. The residence time in the leach bath is preferably less than 14 hours, more preferably less than 2 hours. The residence time in the leach bath is preferably more than 1 second, more preferably more than 30 seconds.

Following leaching, the membrane may optionally be dried. Prior to drying, the leach liquid remaining in the membrane may optionally be exchanged with a more volatile, non-polar drying agent which possesses a low surface tension and is a solvent for the leach liquid and which is a non-solvent for the poly(etheretherketone)-type polymer in order to reduce the possibility of pore collapse during drying. Preferred drying agents include chlorofluorocarbons, for example, FREON 113® chlorofluorocarbon (® trademark of E.I. duPont de Nemours). The exchange may be carried out at temperatures which do not adversely affect the membrane, preferably between 0°C and 100°C. The membrane may be dried in air or an inert gas such as nitrogen. Drying may also be done under vacuum. The membrane may be dried at temperatures at which drying takes place at a reasonable rate and which do not adversely affect the membranes. The drying temperature is preferably between 0°C and 180°C, more preferably between 10°C and 150°C, even more preferably between 15°C and 120°C. The drying time is preferably less than 24 hours, more preferably less than 6 hours. The drying time is preferably at least 30 seconds, more preferably at least 60 seconds.

The membrane may optionally be drawn or stretched subsequent to the quench/coagulation step using conventional equipment such as godets to improve the flux and strength of the membrane. Drawing may occur before leaching, during leaching, after leaching, or a combination thereof. The draw temperature is dependent upon whether the membrane contains plasticizer at the time of drawing. For substantially plasticizer-free membranes, the membrane is drawn at a temperature which is above the glass transition temperature and below the crystalline melting point of the poly(etheretherketone)-type polymer; the minimum temperature at which the membranes are drawn is preferably at least 140°C, more preferably at least 150°C. The maximum temperature at which the membrane is drawn is preferably less than 360°C, more preferably less than 330°C. For membranes containing plasticizer, the membrane is drawn at a temperature between ambient temperature and the melting point of the poly(ether-etherketone)-type polymer or the depressed melting point of the poly(etheretherketone)-type polymer and plasticizer mixture; preferred lower draw temperatures are 25°C or above; preferred upper draw temperatures are less than 10°C below the depressed melting point. The membrane is drawn by stretching the membrane under tension. The membrane is drawn to a ratio of between 1.1 to 40. The draw ratio refers to the ratio of the final length of the membrane after drawing to the original length of the membrane before drawing. The degree of draw may also be expressed as percent elongation, which is calculated by:

$$\frac{L_f - L_i}{L_i} \times 100 \quad ,$$

wherein  $L_f$  is the final length of the membrane after drawing and  $L_i$  is the initial length of the membrane before drawing. Drawing may be carried out in a single step or in a series of steps using the same or different draw ratios in each step.

Line speeds for drawing are not critical and may vary significantly. Practical preferred line speeds range from 10 feet per minute (3 meters per minute) to 2,000 feet per minute (610 meters per minute). In the case of hollow fibers, the drawn fiber preferably possesses an outside diameter of from 10 to 7,000 µm, more preferably of from 50 to 5,000 µm, even more preferably of from 100 to 3,000 µm, with a wall thickness preferably of from 10 to 700 µm, more preferably of from 25 to 500 µm. In the case of films, the film preferably possesses a thickness of from 10 to 700 µm, more preferably of from 20 to 500 µm, even more preferably of from 25 to 250 µm. The films may optionally be supported by a permeable cloth or screen.

Optionally, before leaching, after leaching, before drawing, after drawing, or a combination thereof, the membrane may be annealed by exposing the membrane to elevated temperatures. The membrane may be

annealed at temperatures above the glass transition temperature (T<sub>g</sub>) of the poly(etheretherketone)-type polymer or poly(etheretherketone)-type polymer and plasticizer mixture and 10°C below the melting point of the polymer or depressed melting point of the poly(etheretherketone)-type polymer and plasticizer mixture for a period of time between 30 seconds and 24 hours.

5 The membranes of this invention may be isotropic or anisotropic. Isotropic microporous membranes possess a morphology in which the pore size within the membrane is substantially uniform throughout the membrane. Anisotropic (asymmetric) microporous membranes possess a morphology in which a pore size gradient exists across the membrane; that is, the membrane morphology varies from highly porous, larger pores at one membrane surface to less porous, smaller pores at the other membrane surface. Such  
10 anisotropic membranes thus possess a microporous "skin" of smaller pores. In hollow fiber anisotropic membranes, the "skin" may be on the inside or outside surface of the hollow fiber. The term asymmetric is often used interchangeably with the term anisotropic.

In a preferred embodiment of this invention, the microporous membranes are useful in the treatment of liquids by the membrane separation processes of microfiltration, ultrafiltration, macrofiltration, depth filtra-  
15 tion, membrane stripping, and membrane distillation. Such membranes may also be used as porous supports for composite gas or liquid separation membranes. In an especially preferred embodiment, the microporous membranes are useful for ultrafiltration or microfiltration. Ultrafiltration and microfiltration are pressure driven filtration processes using microporous membranes in which particles or solutes are separated from solutions. Separation is achieved on the basis of differences in particle size or molecular  
20 weight. Macrofiltration is a pressure driven filtration process using microporous membranes to separate particles or solutes having a size greater than 10 microns from solution.

Ultrafiltration and microfiltration membranes may be characterized in a variety of ways, including porosity, mean pore size, maximum pore size, bubble point, gas flux, water flux, molecular weight cut off, and Scanning Electron Microscopy (SEM). Such techniques are well known in the art for characterizing  
25 microporous membranes. See Robert Kesting, Synthetic Polymer Membranes, 2nd edition, John Wiley & Sons, New York, New York, 1985, pp. 43-64; Channing R. Robertson (Stanford University), Molecular and Macromolecular Sieving by Asymmetric Ultrafiltration Membranes, OWRT Report, NTIS No. PB85-1577661EAR, September 1984; and ASTM Test Methods F316-86 and F317-72 (1982).

Porosity refers to the volumetric void volume of the membrane. The membranes must possess  
30 porosities permitting sufficient flux through the membrane while retaining sufficient mechanical strength under use conditions. The membranes of this invention preferably have a porosity of at least 10 percent, more preferably of at least 20 percent, even more preferably of at least 25 percent; the membranes of this invention preferably have a porosity of less than 90 percent, more preferably of less than 80 percent, even more preferably of less than 75 percent.

35 Pore size of the membrane may be estimated by several techniques including Scanning Electron Microscopy (SEM), and/or measurements of bubble point, gas flux, water flux, and molecular weight cut off. The pore size of any given membrane is distributed over a range of pore sizes, which may be narrow or broad.

The bubble point pressure of a membrane is measured by mounting the membrane in a pressure cell  
40 with liquid in the pores of the membrane. The pressure of the cell is gradually increased until air bubbles permeate the membrane. Because larger pores become permeable at lower pressures, the pressure at the first appearance of bubbles is indicative of the maximum pore size of the membrane. If the number of pores which are permeable to air increases substantially with a small increase in pressure, a narrow pore size distribution is indicated. If the number of air-permeable pores increases gradually with increasing pressure,  
45 a broad pore size distribution is indicated. The relationship between pore size and bubble point pressure can be calculated from the equation

$$r = \frac{2G}{P},$$

50 wherein

r is the pore radius,  
G is the surface tension (water/air), and  
P is the pressure.

The mean pore size of the membranes of this invention useful for ultrafiltration is preferably between 5  
55 and 1,000 Angstroms, more preferably between 10 and 500 Angstroms; the maximum pore size of such membranes is preferably less than 100 nm (1,000 Angstroms), more preferably less than 80 nm (800 Angstroms). The mean pore size of the membranes of this invention useful for microfiltration is preferably between 0.02 and 10 μm, more preferably between 0.05 and 5 μm; the maximum pore size of such

membranes is preferably less than 10  $\mu\text{m}$ , more preferably less than 8  $\mu\text{m}$ . The mean pore size of membranes of this invention useful for macrofiltration is preferably between 10 and 50  $\mu\text{m}$ .

Gas flux is defined as

$$F = \frac{(\text{amount of gas passing through the membrane})}{(\text{membrane area})(\text{time})(\text{driving force across the membrane})}.$$

A standard gas flux unit is

$$\frac{(\text{centimeter})^3(\text{STP})}{(\text{centimeter})^2(\text{second})(\text{centimeter Hg})},$$

abbreviated hereinafter as

$$\frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \text{ sec cmHg}},$$

where STP stands for standard temperature and pressure.

The membranes of this invention preferably have a gas flux for nitrogen of at least

$$10^{-6} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \text{ sec cmHg}},$$

more preferably of at least

$$10^{-5} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \text{ sec cmHg}},$$

even more preferably of at least

$$10^{-4} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \text{ sec cmHg}}.$$

Water flux is defined as

$$W = \frac{(\text{amount of water passing through the membrane})}{(\text{membrane area})(\text{time}) (\text{pressure})}$$

under given conditions of temperature and pressure.

The membranes of this invention preferably exhibit a water flux of at least

$$1 \frac{\text{ml}}{\text{m}^2 \text{ hr cmHg}},$$

more preferably of at least

$$10 \frac{\text{ml}}{\text{m}^2 \text{ hr cmHg}},$$

even more preferably of at least

$$100 \frac{\text{ml}}{\text{m}^2 \text{ hr cmHg}}.$$

The membranes are fabricated into flat sheet, spiral wound, tubular, or hollow fiber devices by methods described in the art. Spiral wound, tubular, and hollow fiber devices are preferred. Tubesheets may be affixed to the membranes by techniques known in the art. Preferred tubesheet materials include thermoset and thermoplastic polymers. The membrane is sealingly mounted in a pressure vessel in such a manner that the membrane separates the vessel into two fluid regions wherein fluid flow between the two regions is accomplished by fluid permeating through the membrane. Conventional membrane devices and fabrication procedures are well known in the art.

Ultrafiltration, microfiltration, and macrofiltration are pressure driven filtration processes using microporous membranes to recover or isolate solutes or particles from solutions. The membrane divides the separation chamber into two regions, a higher pressure side into which the feed solution is introduced and a lower pressure side. One side of the membrane is contacted with the feed solution under pressure, while a pressure differential is maintained across the membrane. To be useful, at least one of the particles or solutes of the solution is selectively retained on the high pressure side of the membrane while the remainder of the solution selectively passes through the membrane. Thus the membrane selectively "rejects" at least one type of the particles or solutes in the solution, resulting in a retentate stream being withdrawn from the high pressure side of the membrane which is enriched or concentrated in the selectively rejected particle(s) or solute(s) and a filtrate stream being withdrawn from the low pressure side of the membrane which is depleted in the selectively rejected particle(s) or solute(s).

The separation process should be carried out at pressures which do not adversely affect the membrane, that is, pressures which do not cause the membrane to mechanically fail. The pressure differential across the membrane is dependent upon the membrane characteristics, including pore size and porosity. For the membranes of this invention useful for ultrafiltration or microfiltration, the pressure differential across the membrane is preferably between 134.5 kN/m<sup>2</sup> and 3550 kN/m<sup>2</sup> (5 psig and 500 psig), more preferably between 169 kN/m<sup>2</sup> and 2170 kN/m<sup>2</sup> (10 psig and 300 psig), even more preferably between 272.5 kN/m<sup>2</sup> and 1135 kN/m<sup>2</sup> (25 and 150 psig). For the membranes of this invention useful as supports for composite liquid or gas separation membranes, the pressure differential across the membrane is preferably between 134.5 kN/m<sup>2</sup> and 10450 kN/m<sup>2</sup> (5 psig and 1,500 psig). The separation process should be carried out at temperatures which do not adversely affect membrane integrity. Under continuous operation, the operating temperature is preferably between 0 °C and 300 °C, more preferably between 15 °C and 250 °C, even more preferably between 20 °C and 175 °C.

The following examples are presented for illustrative purposes only and are not intended to limit the scope of the invention or claims.

Example 1 - Solvents and Non-solvents for Poly(etheretherketone) (PEEK).

Poly(etheretherketone) (PEEK), designated as Grade 150P, was obtained from ICI Americas, Inc., Wilmington, Delaware. The PEEK was dried at 150 °C for 16 hours in an air-circulating oven and was stored in a desiccator over Drierite. One hundred seven organic compounds were evaluated for their solvent effect on PEEK. Most of the organic compounds were obtained from Aldrich Chemical Company and used as received. Other organic chemicals were obtained from suppliers as listed in Chemical Sources, published annually by Directories Publishing Co., Inc., of Columbia, South Carolina.

Mixtures of PEEK and a solvent or a non-solvent, a total weight of less than 2 grams, were prepared by weighing PEEK and solvent or non-solvent to a precision of  $\pm 0.001$  gram in a 1 to 4 dram size glass vial. The resulting air space in each vial, which varied considerably due to the large differences in the bulk densities of the compounds, was purged with nitrogen. The vials were sealed with screw caps containing aluminum foil liners. Solubility was usually determined at 10 weight percent polymer, followed by additional determinations at 25 and 50 weight percent if necessary.

In the following tables, in the solubility column, "g" is greater than (>), and "s" is smaller or less than (<), and "=" is equal to.

Table I below lists the solvent effect of 107 organic compounds on PEEK. The approximate solubility of each polymer-organic compound mixture is shown at the indicated temperature(s). Also listed in Table I is an approximate molecular weight, melting point, and boiling point of each organic compound, if these physical properties were available.

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TABLE I

Compound	Approximate				
	Molec. Weight	Melting Point	Boiling Point	Solub. (g = >; s = <)	Temp. (°C)
Triphenylmethanol	260	161	360	g 50.1%?	349
Triphenylmethane	244	93	359	g 50.2%	349
Triphenylene	228	196	438	g 50.0%	350
1,2,3-Triphenylbenzene	306	158	-	g 50.1%	349
1,3,5-Triphenylbenzene	306	173	460	s 9.9%	349
Tetraphenylmethane	320	281	431	=s 10.7%	349
Tetraphenylsilane	337	236	422	s 10.1%	349
Diphenyl sulfoxide	202	70	350	s 10.5%a	349
Diphenyl sulfone	218	124	379	g 50.0%	349
2,5-Diphenyloxazole	221	72	360	g 50.0%	349
Diphenic acid	242	228	-	g 25.1%?a	349
1,1-Diphenylacetone	210	60	-	s 10.0%	302
1,3-Diphenylacetone	210	33	330	s 10.1%	302
4-Acetylbiphenyl	196	117	-	s 10.3%	302
2-Biphenylcarboxylic acid	198	109	349	g 50.1%	349
4-Biphenylcarboxylic acid	198	225	-	g 10.0%	349
4-Biphenylcarboxylic acid	198	225	-	=g 50.1%?	349
m-Terphenyl	230	83	379	g 50.2%	349
m-Terphenyl	230	83	379	s 5.0%	302
4-Benzoylbiphenyl	258	100	419	g 50.1%	349
4-Benzoylbiphenyl	258	100	419	s 5.2%	302
4,4'-Diphenylbenzophenone	334	-	-	s 10.4%	302
1-Benzoyl-4-piperidone	203	56	399	g 9.8%?a	349
2-Benzoylnaphthalene	232	81	383	g 49.9%	349
Diphenyl carbonate	214	79	301	s 10.1%	302

a = Black or very dark color

b = reacts?

\* Monsanto Company

TABLE I

Compound	Approximate				
	Molec. Weight	Melting Point	Boiling Point	Solub. (g = >; s = <)	Temp. (°C)
Bibenzyl	182	51	284	s 10.3%	274
Diphenyl methyl phosphate	264	-	389	s 10.0% <sup>a</sup>	349
1-Bromonaphthalene	207	-1	280	s 9.8%	274
N,N-Diphenylformamide	197	71	337	g 9.9%	302
N,N-Diphenylformamide	197	71	337	s 25.2%	302
3-Phenoxybenzyl alcohol	200	-	329	g 24.7%	302
3-Phenoxybenzyl alcohol	200	-	329	s 49.9%	302
Fluoranthene	202	108	384	g 50.0%	349
2-Phenoxybiphenyl	246	49	342	s 10.9%	302
Triphenyl phosphate	326	51	281	s 9.9%	274
Cyclohexyl phenyl ketone	188	56	-	s 9.9%	302
2,5-Diphenyl-1,3,4-oxadiazole	222	139	382	g 49.9%	349
1,4-Dibenzoylbutane	266	107	-	s 10.0%	302
9-Fluorenone	180	83	342	g 24.9%	302
9-Fluorenone	180	83	342	s 50.0%	302
1,2-Dibenzoyl benzene	286	146	-	g 50.2%	349
Dibenzoylmethane	224	78	360	g 50.4%	349
2,4,6-Trichlorophenol	197	65	246	s 9.0%	240
Benzil	210	94	347	g 10.2%	302
Benzil	210	94	347	s 25.0%	302
p-Terphenyl	230	212	389	s 9.8%	302
p-Terphenyl	230	212	389	g 50.0%	349
Anthracene	178	216	340	g 10.0%	302
Anthracene	178	216	340	s 24.7%	302
Mineral oil	-	-	360	s 10.7%	349

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\* Monsanto Company

TABLE I

Compound	Approximate				
	Molec. Weight	Melting Point	Boiling Point	Solub. (g = >; s = <)	Temp. (°C)
Butyl stearate	341	-	343	s 10.0%	302
9-Phenylanthracene	254	151	417	g 10.4% <sup>a</sup>	349
1-Phenylanthracene	204	-	324	g 9.9%	302
1-Phenylanthracene	204	-	324	s 25.0%	302
4-Phenylphenol	170	166	321	g 25.8%	297
4-Phenylphenol	170	166	321	s 50.0%	302
4-Phenylphenol	170	166	321	g 50.0%	304
2-Phenylphenol	170	59	282	s 10.2%	274
1-Ethoxynaphthalene	172	-	280	s 10.2%	274
Phenyl benzoate	198	69	298	s 9.8%	274
1-Phenyldecane	218	-	293	s 10.2%	274
1-Methoxynaphthalene	158	-	269	s 10.0%	240
2-Methoxynaphthalene	158	74	274	s 9.4%	240
4-Bromobiphenyl	233	86	310	g 5.2%	300
4-Bromobiphenyl	233	86	310	s 24.8%	302
4-Bromobiphenyl	233	86	310	s 5.2%	241
4-Bromodiphenyl ether	249	18	305	=g 5.4%	300
4-Bromodiphenyl ether	249	18	305	s 24.8%	302
4-Bromodiphenyl ether	249	18	305	s 5.4%	241
1,3-Diphenoxybenzene	262	60	-	=s 5.4% <sup>a</sup>	300
1,3-Diphenoxybenzene	262	60	-	s 5.4% <sup>a</sup>	241
1,8-Dichloroanthraquinone	277	202	-	s 5.3% <sup>a</sup>	300
1,8-Dichloroanthraquinone	277	202	-	s 5.3% <sup>a</sup>	241
9,10-Dichloroanthracene	247	214	-	s 5.5% <sup>a</sup>	300
4,4'-Dibromobiphenyl	312	170	355	s 5.2%	241

a = Black or very dark color

b = reacts?

\* Monsanto Company



TABLE I

Compound	Approximate				
	Molec. Weight	Melting Point	Boiling Point	Solub. (g = >; s = <)	Temp. (°C)
4,4'-Dibromobiphenyl	312	170	355	g 5.2%	300
4,4'-Dibromobiphenyl	312	170	355	s 25.1%	302
4,4'-Dibromobiphenyl	312	170	355	g 50.1%	349
Benzophenone	182	50	305	s 11.3%	241
Benzophenone	182	50	305	=g 11.3%	300
Benzophenone	182	50	305	s 24.9%	302
Polyphosphoric acid	-	-	-	s 4.8%a	300
1-Chloronaphthalene	162	-20	258	s 9.9%	241
Diphenyl ether	170	27	259	s 10.1%	241
1-Cyclohexyl-2-pyrrolidinone	167	-	302	=s 10.0%a	300
1-Benzyl-2-pyrrolidinone	175	-	-	g 14.9%	302
1-Benzyl-2-pyrrolidinone	175	-	-	s 32.9%	302
o,o'-Biphenol	186	109	315	s 5.1%	221
o,o'-Biphenol	186	109	315	g 9.8%	302
o,o'-Biphenol	186	109	315	s 25.0%	302
HB-40 (hydrogenated terphenyl) *	244	-	325	s 9.9%	302
Diethyl phthalate	391	-50	384	s 10.8%	349
5-Chloro-2-benzoxazolone	170	191	-	s 10.2%a	349
Dibenzothiophene	184	98	332	g 10.3%?b?	302
Bis(4-chlorophenyl sulfone)	287	146	412	s 15.3%	349
Diphenyl phthalate	318	79.5	-	g 50.0%	349
2,6-Diphenylphenol	246	101	-	g 50.0%	349
Diphenyl sulfide	186	-40	296	s 9.0%	274
Diphenyl chlorophosphate	269	-	360	s 9.9%	349

a = Black or very dark color

b = reacts?

\* Monsanto Company

TABLE I

Compound	Approximate				
	Molec. Weight	Melting Point	Boiling Point	Solub. (g = >; s = <)	Temp. (°C)
Fluorene	166	113	298	s 10.1%	274
Phenanthrene	178	100	340	g 10.0%	302
Phenanthrene	178	100	340	s 25.0%	302
Sulfolane	120	27	285	s 10.1%	274
Methyl myristate	242	18	323	s 8.2%	302
Methyl stearate	299	38	358	s 10.1%	349
Phenothiazine	199	182	371	g 49.9%	349
Hexadecane	226	19	288	s 10.0%	274
Dimethyl phthalate	194	2	282	s 10.0%	274
Tetraethylene glycol dimethyl ether	222	-30	275	s 9.6%	240
Diethylene glycol dibutyl ether	218	-60	256	s 9.6%	240
Docosane	311	44	369	s 10.4%	349
Eicosane	283	37	340	s 7.9%	302
Dotriacontane	451	70	476	s 10.4%	349
2,7-Dimethoxynaphthalene	188	138	-	g 10.0%ab	349
2,6-Dimethoxynaphthalene	188	153	-	g 10.8%b	349
o-Terphenyl	230	58	337	s 9.9%	302
4,4'-Dimethoxy-benzophenone	242	142	-	g 50.0%	349
9,10-Diphenylanthracene	330	246	-	g 50.0%	349
1,1-Diphenylethylene	180	6	270	s 9.7%	240
epsilon-Caprolactam	113	71	271	s 10.0%	240
Tetraphenylethylene	332	223	420	s 10.9%	302
Pentafluorophenol	184	35	143	s 9.9%	140

a = Black or very dark color

b = reacts?

\* Monsanto Company

TABLE I

Compound	Approximate				
	Molec. Weight	Melting Point	Boiling Point	Solub. (g = >; s = <)	Temp. (°C)
Pentafluorophenol	184	35	143	g 5.0%	141
Thianthrene	216	158	365	s 10.2%	302
Pentachlorophenol	266	189	310	g 25.0%	302
Pentachlorophenol	266	189	310	s 50.6%	302
Pyrene	202	150	404	g 50.0%	347
Benzanthrone	230	169	-	s 25.5% <sup>ab</sup>	328
9,9'-Bifluorene	330	247	-	g 25.2%	327
9,9'-Bifluorene	330	247	-	s 50.2%	318
9,9'-Bifluorene	330	247	-	g 50.2%	327
Santowax R * Chem Abstr. #26140-60-3	-	145	364	g 60.0%	347
Therminol 66 * Chem Abstr. #61788-32-7	240	-	340	g 50.1%	337
Therminol 75 * Chem Abstr. #26140-60-3 Chem Abstr. #217-59-4	-	70	385	g 24.9%	325
Therminol 75 *	-	70	385	g 50.3%	332
1-Phenyl-2-pyrrolidinone	161	68	345	g 10.1%	279
1-Phenyl-2-pyrrolidinone	161	68	345	g 25.5%	290
1-Phenyl-2-pyrrolidinone	161	68	345	g 50.0%	317
4,4'-Isopropylidenediphenol	228	156	402	=g 50.0%	301
4,4'-Isopropylidenediphenol	228	156	402	g 50.0%	318
4,4'-Dihydroxy-benzo-phenone	214	214	-	s 10.0%	301
4,4'-Dihydroxy-benzo-phenone	214	214	-	g 25.0%	310
4,4'-Dihydroxy-benzo-phenone	214	214	-	s 50.0%	319

a = Black or very dark color

b = reacts?

\* Monsanto Company

Example 2 - Microporous Poly(etheretherketone) Membranes From Poly(etheretherketone), Poly-(caprolactone), And Diphenylsulfone.

Microporous poly(etheretherketone) (PEEK) film membranes were prepared from a mixture of PEEK, poly(caprolactone), and diphenylsulfone using the following procedure.

A mixture of 50 weight percent poly(etheretherketone), VICTREX™ 450P (™ trademark of ICI Americas, Inc.), and 50 weight percent diphenylsulfone was compounded, extruded, and pelletized using a twin screw extruder, a die temperature of 305°C to 310°C, and an extrusion rate of 17.5 to 18.5 grams/minute. The resulting pellets had a composition of 53 weight percent PEEK as measured by thermogravimetric analysis (TGA) at a heating rate of 20°C/minute under nitrogen.

The PEEK/diphenylsulfone pellets thus obtained were mixed with poly(caprolactone) pellets, CAPA™ 650 (™ trademark of Interlox Chemicals Ltd.) in a weight ratio of 40 percent PEEK, 40 percent diphenylsulfone, and 20 percent poly-(caprolactone). The mixture of pellets was extruded into a film using a twin screw extruder equipped with a 2.25 inch (5.72 centimeter) wide film die at an extrusion temperature (die temperature) of 310°C and an extrusion rate of 40 grams/minute. The extruded film was taken up on a chilled godet. The draw ratio varied from 1 to 3. The actual composition of the extruded film as measured by TGA at a heating rate of 5°C/minute under vacuum was 42.5 weight percent PEEK, 36.7 weight percent diphenylsulfone, and 20.8 weight percent poly(caprolactone).

The diphenylsulfone and poly(caprolactone) were leached from the film by immersing the film in an acetone bath at room temperature for 1 hour and vacuum drying the film for 2 hours. The film was then immersed in a toluene bath at room temperature for 1 hour and vacuum dried overnight.

The maximum pore size of the film as measured by Scanning Electron Microscopy was 30 μm. Samples of the film, each with an effective surface area of 3.46 square centimeters, were evaluated for nitrogen flux and water flux at room temperature as reported in Table II.

TABLE II

Sample	Draw Ratio	Thickness (millimeters)	Nitrogen Flux $\frac{\text{cm}^3}{\text{cm}^2 \text{ sec cmHg}}$	Water Flux $\frac{\text{cm}^3}{\text{m}^2 \text{ hr cmHg}}$
A1	1	0.471	1.37	$1.53 \times 10^7$
A2	1	0.495	1.38	$1.20 \times 10^7$
B1	2	0.241	1.45	$3.04 \times 10^7$
B2	2	0.278	1.33	$2.77 \times 10^7$
C1	2.3	0.202	1.51	$6.74 \times 10^7$
C2	2.3	0.223	1.43	$5.74 \times 10^7$
D1	2.7	0.172	1.43	$7.05 \times 10^7$
D2	2.7	0.177	1.50	$5.96 \times 10^7$
E1	3	0.175	1.59	$6.74 \times 10^7$
E2	3	0.214	1.59	$6.46 \times 10^7$
F1	1.7	0.235	1.47	$3.74 \times 10^7$
F2	1.7	0.243	1.41	$3.83 \times 10^7$

#### Example 3 - Microporous Poly(etheretherketone) Membranes From Poly(etheretherketone) And Poly-(caprolactone).

Microporous poly(etheretherketone) (PEEK) film membranes were prepared from a mixture of PEEK, VICTREX™ 150P (™ trademark of ICI Americas, Inc.), 80 weight percent, and poly(caprolactone), CAPA™

650 (™ trademark of Interlox Chemicals Ltd.), 20 weight percent, using a twin screw extruder equipped with a 2.25 inch (5.72 centimeter) wide film die. The film was extruded at a temperature of 340°C (die temperature). The extruded film was taken up on a chilled godet. The extruded film had a composition of 81.6 weight percent PEEK and 18.4 weight percent poly(caprolactone) as measured by thermogravimetric analysis at a heating rate of 20°C/minute under vacuum. The film was subsequently leached in toluene at room temperature for 2 hours and dried under vacuum. The film had a maximum pore size of 0.42 μm at a pressure of 151.8 kN/m<sup>2</sup> (22 psi) and a mean pore size of 0.051 μm at a pressure of 1242 kN/m<sup>2</sup> (180 psi) as determined by the bubble point method. A sample of the film, having an effective surface area of 3.46 square centimeters, was evaluated for nitrogen flux and water flux at room temperature as reported in Table III.

TABLE III

Thickness (millimeters)	Nitrogen Flux $\frac{\text{cm}^3}{\text{cm}^2 \text{ sec cmHg}}$	Water Flux $\frac{\text{cm}^3}{\text{m}^2 \text{ hr cmHg}}$
0.394	$3.84 \times 10^{-3}$	235

Example 4 - Microporous Poly(etheretherketone) Membranes From Poly(etheretherketone), Poly(caprolactone). And Diphenylsulfone.

Microporous poly(etheretherketone) (PEEK) film membranes were prepared from a mixture of PEEK, poly(caprolactone), and diphenylsulfone using the following procedure.

A mixture of 50 weight percent poly(etheretherketone), VICTREX™ 450P (™ trademark of ICI Americas, Inc.), and 50 weight percent diphenyl-sulfone was compounded, extruded, and pelletized using a twin screw extruder, and a die temperature of 310°C.

The PEEK/diphenylsulfone pellets thus obtained were mixed with poly(caprolactone) pellets, CAPA™ 650 (™ trademark of Interlox Chemicals Ltd.) in a weight ratio of 42.5 percent PEEK, 42.5 percent diphenylsulfone, and 15 percent poly(caprolactone). The mixture of pellets was extruded into a film using a twin screw extruder equipped with a 2.25 inch (5.72 centimeter) wide film die at an extrusion temperature (die temperature) of 310°C. The extruded film was taken up on a chilled godet. The actual composition of the extruded film as measured by TGA at a heating rate of 5°C/minute under vacuum was 49.7 weight percent PEEK, 36.9 weight percent diphenylsulfone, and 13.4 weight percent poly(caprolactone).

The diphenylsulfone and poly(caprolactone) were leached from the film by immersing the film in an acetone bath at room temperature for 2 hours and vacuum drying the film. The film was then immersed in a toluene bath at room temperature for 2 hours and vacuum dried.

The maximum pore size of the film as measured by the bubble point method was 4.6 μm at 13.8 kN/m<sup>2</sup> (2 psi); the mean pore size of the film as measured by the bubble point method was 1.3 μm at 48.3 kN/m<sup>2</sup> (7 psi). Samples of the film, each with an effective surface area of 3.46 square centimeters, were evaluated for nitrogen flux and water flux at room temperature. The average nitrogen flux was

$$5.0 \times 10^{-1} \frac{\text{cm}^3}{\text{cm}^2 \text{ sec cmHg}}$$

at 25 °C and the average water flux was

$$37,100 \frac{\text{ml}}{\text{m}^2 \text{ hr cmHg}}$$

at 25 °C.

# Claims

1. A process for preparing a microporous membrane from an unsulfonated poly(etheretherketone)-type polymer comprising the steps of:
  - A. forming a mixture comprising:
    - (i) at least one unsulfonated poly(etheretherketone)-type polymer, and
    - (ii) at least one low melting point crystallizable polymer which is at least partially incompatible with said poly(etheretherketone)-type polymer and which possesses a melting point of less than (T<sub>m</sub> - 30 °C), wherein T<sub>m</sub> is the melting point of said poly(etheretherketone)-type polymer, and a molecular weight of at least 400;
  - B. heating said mixture to a temperature at which said mixture becomes a fluid; and
  - C. extruding or casting said fluid under conditions such that a membrane is formed.
2. The process of Claim 1 wherein the mixture further comprises:
  - a plasticizer comprising at least one organic compound capable of dissolving at least 10 weight percent of said poly(etheretherketone)-type polymer at the extrusion or casting temperature.
3. The process of Claims 1 or 2 which further comprises the additional step of:
  - D. quenching or coagulating said membrane by passing said membrane through at least one zone under conditions such that said membrane solidifies.
4. The process of Claim 3 which further comprises the additional step of:
  - E. leaching said membrane by passing said membrane through at least one zone under conditions such that at least a portion of said low melting point crystallizable polymer, at least a portion of said plasticizer for the poly(etheretherketone)-type polymer, or a combination thereof, is removed from said membrane.
5. The process of Claim 4 which further comprises the additional step of:
  - F. before leaching, during leaching, after leaching, or a combination thereof, drawing said membrane to increase the flux of fluid through said membrane, while said membrane is at a temperature above 25 °C and below the melting point of the poly(etheretherketone)-type polymer or the depressed melting point of said mixture.
6. The process of Claim 1 wherein said poly(etheretherketone)-type polymer is selected from the group consisting of poly(etherketone), poly(aryletherketone), poly(etheretherketone), poly(etherketoneketone), poly(etheretheretherketone), poly(etheretherketoneketone), poly(etherketoneetherketoneketone), and mixtures thereof.
7. The process of Claim 1 wherein said low melting point crystallizable polymer is selected from the group consisting of poly(caprolactones), poly(ethylene oxide), poly(ethylene glycol), poly-(oxymethylene), poly(trimethylene oxide), poly(ethylene glycol)methylether, poly(vinyl alcohol), poly-(vinyl chloride), crystalline cellulose esters, poly(caprolactone)diol, and poly(caprolactone)triol.
8. The process of Claim 2 wherein said plasticizer comprises at least one solvent consisting predominantly of carbon and hydrogen and optionally oxygen, nitrogen, sulfur, halogen, and mixtures thereof, wherein the solvent has a molecular weight of between 160 and 450, contains at least one six-membered ring structure, and possesses a boiling point of between 150 °C and 480 °C.

9. The process of Claim 1 wherein the amount of poly(etheretherketone)-type polymer in said mixture is between 10 and 90 weight percent.

# Patentansprüche

5

1. Verfahren zur Herstellung einer mikroporösen Membran aus einem nichtsulfo­nierten Polymerem vom Poly(etheretherketon)-typ, umfassend die Stufen von:

A. Bildung einer Mischung, welche umfaßt:

10

- (i) wenigstens ein nichtsulfo­niertes Polymeres vom Poly(etheretherketon)-typ, und  
(ii) wenigstens ein kristallisierbares Polymeres mit niedrigem Schmelzpunkt, das wenigstens teilweise mit diesem Polymeren vom Poly(etheretherketon)-typ nichtverträglich ist und einen Schmelzpunkt von weniger als ( $T_m - 30^\circ \text{C}$ ) besitzt, wobei  $T_m$  der Schmelzpunkt dieses Polymeren vom Poly(etheretherketon)-typ ist, und das ein Molekulargewicht von wenigstens 400 hat;

15

- B. Erhitzen dieser Mischung auf eine Temperatur, bei welcher diese Mischung ein Fluid wird; und  
C. Extrudieren oder Gießen dieses Fluids unter solchen Bedingungen, daß eine Membran gebildet wird.

20

2. Verfahren nach Anspruch 1, worin die Mischung weiter umfaßt: einen Weichmacher, umfassend wenigstens eine organische Verbindung, die zum Auflösen von wenigstens 10 Gew.-% dieses Polymeren vom Poly(etheretherketon)-typ bei der Extrusions- oder Gießtemperatur fähig ist.

25

3. Verfahren nach Anspruch 1 oder 2, welches weiter die zusätzliche Stufe umfaßt von:  
D. Abschrecken oder Koagulieren dieser Membran durch Durchführen der Membran durch wenigstens eine Zone unter solchen Bedingungen, daß die Membran sich verfestigt.

30

4. Verfahren nach Anspruch 3, welches weiter die zusätzliche Stufe umfaßt von:  
E. Auslaugen dieser Membran durch Durchführen dieser Membran durch wenigstens eine Zone unter solchen Bedingungen, daß wenigstens ein Teil dieses kristallisierbaren Polymeren mit niedrigem Schmelzpunkt, wenigstens ein Teil dieses Weichmachers für das Polymere vom Poly(etheretherketon)-typ oder eine Kombination hiervon aus dieser Membran entfernt wird.

35

5. Verfahren nach Anspruch 4, welches weiter die zusätzliche Stufe umfaßt von:  
F. vor dem Auslaugen, während des Auslaugens oder nach dem Auslaugen oder einer Kombination hiervon das Ziehen der Membran zur Erhöhung des Fluidflusses durch diese Membran, während sich diese Membran auf einer Temperatur oberhalb  $25^\circ \text{C}$  und unterhalb des Schmelzpunktes des Polymeren vom Poly(etheretherketon)-typ oder des erniedrigten Schmelzpunktes dieser Mischung befindet.

40

6. Verfahren nach Anspruch 1, worin dieses Polymere vom Poly(etheretherketon)-typ ausgewählt wird aus der aus Poly(etherketon), Poly(aryletherketon), Poly(etheretherketon), Poly(etherketonketon), Poly(etheretheretherketon), Poly(etheretherketonketon), Poly(etherketonetherketonketon) und Mischungen hiervon bestehenden Gruppe.

45

7. Verfahren nach Anspruch 1, worin dieses kristallisierbare Polymere mit niedrigem Schmelzpunkt ausgewählt ist aus der aus Poly(caprolactonen), Poly(ethylenoxid), Poly(ethylenglykol), Poly(oxymethylen), Poly(trimethylenoxid), Poly(ethylenglykol)methylether, Poly(vinylalkohol), Poly(vinylchlorid), kristallinen Celluloseestern, Poly(caprolacton)-diol und Poly(caprolacton)-triol bestehenden Gruppe.

50

8. Verfahren nach Anspruch 2, worin dieser Weichmacher wenigstens ein Lösungsmittel umfaßt, das überwiegend aus Kohlenstoff und Wasserstoff und wahlweise Sauerstoff, Stickstoff, Schwefel, Halogen und Mischungen hiervon besteht, wobei das Lösungsmittel ein Molekulargewicht zwischen 160 und 450 besitzt, wenigstens eine sechsgliedrige Ringstruktur enthält und einen Siedepunkt zwischen  $150^\circ \text{C}$  und  $480^\circ \text{C}$  besitzt.

55

9. Verfahren nach Anspruch 1, worin die Menge von Polymerem vom Poly(etheretherketon)-typ in dieser Mischung zwischen 10 und 90 Gew.-% beträgt.

# Revendications

1. Procédé de préparation d'une membrane microporeuse à partir d'un polymère de type poly(éther éther cétone) non-sulfoné, procédé qui comporte les étapes consistant à :
  - 5 A) former un mélange comprenant :
    - (i) au moins un polymère de type poly(éther éther cétone) non-sulfoné, et
    - (ii) au moins un polymère cristallisable à bas point de fusion, qui est au moins partiellement incompatible avec ledit polymère de type poly(éther éther cétone) et dont le point de fusion est inférieur à  $T_f - 30^\circ\text{C}$ ,  $T_f$  étant le point de fusion du polymère de type poly (éther éther cétone), et  
10 dont la masse moléculaire vaut au moins 400 ;
  - B) chauffer ce mélange jusqu'à une température à laquelle ce mélange devient un fluide ;
  - C) soumettre ce fluide à une extrusion ou à une coulée, dans des conditions telles qu'il se forme une membrane.
- 15 2. Procédé conforme à la revendication 1, dans lequel le mélange comprend en outre un plastifiant comprenant au moins un composé organique capable de dissoudre au moins 10 % en poids du polymère de type poly(éther éther cétone) à la température d'extrusion ou de coulée.
3. Procédé conforme à la revendication 1 ou 2, qui comporte en outre l'étape supplémentaire consistant à  
20 :
  - D. tremper cette membrane ou la faire coaguler, en la faisant passer dans au moins une zone dans des conditions telles que ladite membrane se solidifie.
4. Procédé conforme à la revendication 3, qui comporte en outre l'étape supplémentaire consistant à :  
25
  - E) lessiver cette membrane en lui faisant traverser au moins une zone dans des conditions telles que soit retirée de cette membrane au moins une partie dudit polymère cristallisable à bas point de fusion, au moins une partie dudit plastifiant utilisé pour le polymère de type poly(éther éther cétone), ou une combinaison des deux.
- 30 5. Procédé conforme à la revendication 4, qui comporte en outre l'étape supplémentaire consistant à :
  - F) avant, pendant, après le lessivage ou en plusieurs de ces moments, étirer ladite membrane pour augmenter le flux de fluide passant à travers elle, alors que la membrane se trouve à une température supérieure à  $25^\circ\text{C}$ , mais inférieure au point de fusion cristalline du polymère de type poly(éther éther cétone) ou au point de fusion abaissé dudit mélange.
- 35 6. Procédé conforme à la revendication 1, dans lequel ledit polymère de type poly(éther éther cétone) est choisi dans l'ensemble constitué par les poly(éther cétone), les poly(aryléther cétone), les poly(éther éther cétone), les poly(éther cétone cétone), les poly(éther éther éther cétone), les poly(éther éther cétone cétone), les poly(éther cétone éther cétone cétone), et leurs mélanges.
- 40 7. Procédé conforme à la revendication 1, dans lequel ledit polymère cristallisable à bas point de fusion est choisi dans l'ensemble constitué par les polycaprolactones, les poly(éthylène oxyde), les polyéthylène glycols, les polyoxyméthylènes, les poly(triméthylène oxyde), les éthers méthyliques de polyéthylène glycols, les poly(alcool vinylique), les poly(chlorure de vinyle), les esters de cellulose cristallins, les poly(caprolactone)diols et les poly(caprolactone)triols.
- 45 8. Procédé conforme à la revendication 2, dans lequel ledit plastifiant comprend au moins un solvant constitué de façon prédominante de carbone et d'hydrogène, et éventuellement, d'oxygène, d'azote, de soufre, d'un halogène ou d'un mélange de ces éléments, et dans lequel le solvant présente une masse molaire située entre 160 et 450, contient au moins une structure cyclique à 6 chaînons et présente un point d'ébullition situé entre  $150^\circ\text{C}$  et  $480^\circ\text{C}$ .
- 50 9. Procédé conforme à la revendication 1, dans lequel la proportion de polymère de type poly(éther éther cétone) dans ledit mélange vaut entre 10 et 90 % en poids.

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